


Racemization of Valine by Impact-Induced Heating

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Abstract Homochirality plays an important role in all living organisms but its origin remains unclear. It also remains unclear whether such chiral molecules survived terrestrial heavy impact events. Impacts of extraterrestrial objects on early oceans were frequent and could have affected the chirality of oceanic amino acids when such amino acids accumulated during impacts. This study investigated the effects of shock-induced heating on enantiomeric change of valine with minerals such as olivine ($[\text{Mg}_{0.9}, \text{Fe}_{0.1}]_2\text{SiO}_4$), hematite (Fe_2O_3), and calcite (CaCO_3). With a shock wave generated by an impact at ~ 0.8 km/s, both D- and L-enriched valine were significantly decomposed and partially racemized under all experimental conditions. Different minerals had different shock impedances; therefore, they provided different P-T conditions for identical impacts. Furthermore, the high pH of calcite promoted the racemization of valine. The results indicate that in natural hypervelocity impacts, amino acids in shocked oceanic water would have decomposed completely, since impact velocity and the duration of shock compression and heating are typically greater in hypervelocity impact events than those in experiments. Even with the shock wave by the impact of small and decelerated projectiles in which amino acids survive, the shock heating may generate sufficient heat for significant racemization in shocked oceanic water. However, the duration of shock induced heating by small projectiles is limited and the population of such decelerated projectiles would be limited. Therefore, even though impacts of asteroids and meteorites were frequent on the prebiotic Earth, impact events would not have significantly changed the ee of proteinogenic amino acids accumulated in the entire ocean.

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Introduction

Biological homochirality is commonly found in biopolymers (e.g., proteins and nucleic acids); however, its origin remains unclear. Homochirality plays a significant role in constructing ordered biopolymers, as seen in the secondary structure of proteins and in the regular distance in the base sequence of nucleic acids. On this basis, homochirality would have been inherent to terrestrial life from its beginning. However, it remains unclear whether homochirality originated from the building blocks of life (e.g., amino acids and sugars) or occurred through polymerization processes.

Several processes have been proposed for the formation and amplification of enantiomeric excess (ee; (Blackmond 2011; Soai et al. 1995; Yun and Gellman 2015). The amino acids and polyols in several carbonaceous chondrites have shown surprising conformity of their ee to biological chirality (i.e., L-enantiomers of amino acids and D-enantiomers of polyols; (Cooper and Rios 2016; Cronin and Pizzarello 1997; Pizzarello and Groy 2011; Pizzarello et al. 2010), which clearly indicates that the abiotic chemical processes that form ee in the building blocks of life were present before the emergence of life.

In the course of chemical evolution, amino acids would have accumulated in the early oceans. Impact-induced heating was common for oceanic water on the early Earth since asteroid/meteorite impacts were far more frequent at that time (Culler et al. 2000; Hartmann et al. 2000; Valley et al. 2002). The impact of projectiles causes flash heating and exerts high pressure on the surface water of the ocean through the traversal of a shock wave. This shock wave propagates through the ocean but diminishes when a rarefaction wave reaches the shock wave. Shock compression and heating generates a number of chemical reactions, including the formation and destruction of amino acids (Bertrand et al. 2009; Blank et al. 2001; Furukawa et al. 2015; Furukawa et al. 2009; Sugahara and Mimura 2014; Suzuki et al. 2015; Umeda et al. 2016). It is clear that the heating of chiral amino acid solutions, having a hydrogen atom on the α -carbon atom results in racemization that reduces the ee (Bada 1972; Smith and Sivakua 1983). All proteinogenic amino acids having a hydrogen atom on the α -carbon tend to be racemized. It remains unclear whether such impact events completely racemize chiral proteinogenic amino acids in oceans when such amino acids were provided during impacts.

Bertrand et al. (2009) reported on impact-induced destruction and racemization of amino acids with low water/rock ratio, simulating the shock-induced reactions of amino acids in meteorites. However, the effects of enantiomeric changes in impact-induced heating of oceanic impacts have not been well investigated. The potential importance of minerals in enantiomeric change has been extensively discussed (Fasel et al. 2006; Orme et al. 2001; Pizzarello and Groy 2011). In this study, we considered the effects of impact-induced heating on the ee of a proteinogenic amino acid, valine, in the presence of several meteoritic and terrestrial minerals (i.e., olivine, calcite, and hematite).

Methods

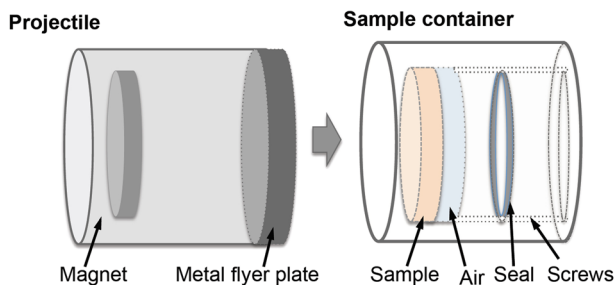
We used commercial valine as a representative amino acid because it less easily contaminates analytical systems than do glycine and alanine. Olivine is a major mineral in most stony

meteorites. Calcite represents a typical mineral in marine shallow sediments. Hematite was used for reference. A natural olivine ($[\text{Fe}_{0.9}\text{Fa}_{0.1}]_2\text{SiO}_4$) from San Carlos was powdered, along with synthetic red hematite powder (99.9%; Wako Chemicals), calcite powder (>99.5%; Kishida Chemicals), and powdered natural calcite (Creel, Chihuahua, Mexico). These powders also acted to control oxygen fugacity during experiments. Olivine contains ferric iron and provides low oxygen fugacity when the reaction system reaches redox equilibrium. Hematite and calcite offer high oxygen fugacities. We used commercially available powders of L-valine (Sigma-Aldrich) and D-valine (Nacalai Tesque). The contents of the L and D forms in the starting materials were more than 98% purity and 99% ee.

Sample solutions of L- and D-valine in sealed steel containers were subjected to impact at velocities of ~ 1 km/s. Hypervelocity plane impact experiments were carried out using a propellant gun at the National Institute for Materials Science (Sekine 1997). The calculated shock pressures were 4.4–8.1 GPa, as based on the impedance match solution using known relationships between shock velocity and particle velocity (Marsh 1980). The details of shock recovery experiments are given in (Sekine 1997). The materials used for the flyer and sample container were stainless steel 304. In most experiments, 200 mg of mineral solid and 130 mL of aqueous solution were used. To seal the solution in the container, we used two copper screws and a soft metal sealant (Pb) on the corner edge between the two screws (Fig. 1). Seal conditions were checked by measuring the weight loss of the containers after they had been kept under vacuum for 1 h. Containers with a weight loss of more than 30 mg were not used for impact experiments.

Recovered sample containers were cleaned thoroughly and kept in liquid nitrogen to freeze the solutions for about 10 min. After the sample solution was frozen, small holes were drilled from the impact surface into the sample cavity at liquid nitrogen temperature. The frozen container was then immersed into a limited amount of pure water (30–50 ml) and left overnight to collect water-soluble products in the post-shock solution at room temperature. The recovered solutions, as well as the starting valine aqueous solutions, were analyzed with a liquid chromatography-mass spectrometer (LC/MS; 2695 separation module and Quattro micro API; Waters; (Furukawa et al. 2009) using the the 1-fluoro-2,4-dinitrophenyl-5-L-leucine-amide (FDLA) derivatization, which differentiates between hydrophobicity in D- and L-valine derivatives (Fujii et al. 1997a; Fujii et al. 1997b). The content was determined against the calibration using standard solutions. Valine yield ($\% \text{ valine} = 100 \frac{[\text{L} + \text{D}]_{\text{product}}}{[\text{L} + \text{D}]_{\text{initial}}}$) was represented as a function of shock pressure, and the relationship between yield and enantiomeric excess ($\% \text{ ee} = 100 \frac{[\text{L} - \text{D}]_{\text{product}}}{[\text{L} + \text{D}]_{\text{product}}}$) was checked to observe change caused by the impact process. It should be noted that ee is independent on the yield. Initial ee

Fig. 1 Schematic illustration of shock recovery experiments. A hypervelocity projectile with front metal flyer impacts a target sample container. The sample is sealed with a soft metal ring sandwiched by the corner edges of two screws. Projectile velocity is measured using a small magnet imbedded in the projectile just before impact



values for the starting L- and D-valine solutions were +100% and -100%, respectively. Mineral combinations were analyzed with x-ray powder diffraction (XRD) equipped with a Cu target.

Results

In this study we used 25 samples: 11 for D-valine, 11 for L-valine, two for a racemic solution, and a control sample (Table 1). Despite almost identical impact velocities, samples had different impact pressures owing to differences in the shock impedance of minerals (Fig. 2). Yields were below 20% in most shock-recovered samples, showing a slight dependence on pressure (Fig. 2). The yields of samples not subjected to impacts were ~80%. Taking this into account, we estimated that sample loss during recovery was ~20%.

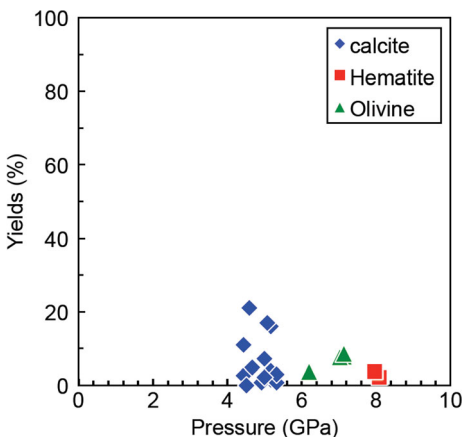
Enantiomeric excess is not affected by sample loss during the extraction process since both L-valine and D-valine behave the same during extraction and analytical processes. In the impact of 0.87 ± 0.01 km/s (number of data; $n = 4$) with calcite, the ee of L-valine decreased from 100 to $66 \pm 5\%$, whereas in the impact of 0.87 ± 0.02 km/s ($n = 4$) with calcite, the ee of D-valine increased from -100 to $-69 \pm 10\%$. This result shows that both enantiomers partially racemized and that there was no significant difference in the extent of the racemization. The ee of L-valine in the experiments with olivine decreased from 100 to 92% following impact at 0.86 km/s ($n = 2$), whereas the ee of D-valine decreased from -100 to -91% following impact

Table 1 Sample compositions, impact conditions, and enantiomer yields

ID	Initial (mM)		Solid	Impact V (km/s)	P (GPa)	Recovered sample (mM)				Yield (%)		ee (%)	
	L	D				L	±	D	±	±	±		
VL4	106	0.03	Cal	0.78	4.4	2	0.1	0.7	0.01	2.6	0.1	48	0.8
VL6	101	0.03	Cal	0.87	5.2	3.2	0.1	0.57	0.01	3.7	0.1	70	1
VL7	101	0.03	Cal	0.87	5.2	1.2	0.02	0.28	0.01	1.5	0.1	62	1.1
VL8	108	0.03	Cal	0.87	5.2	13	1	2.5	0.1	16	0.9	68	3.4
VL9	109	0.03	Cal	0.87	5.2	3.5	0.3	0.61	0.01	3.9	0.2	72	4.2
VL10	102	0.03	Cal	0.85	5.0	5.5	0.4	1.4	0.1	7.2	0.4	57	2.7
VD4	0.02	121	Cal	0.84	4.9	0.11	0.01	0.68	0.01	0.7	0.1	-72	2.4
VD6	0.01	101	Cal	0.89	5.3	0.06	0.01	0.69	0.01	0.8	0.1	-84	2.9
VD7	0.01	105	Cal	0.89	5.3	0.65	0.05	2.4	0.1	3	0.1	-57	1.2
VD8	0.01	101	Cal	0.78	4.4	1.1	0.1	7.5	0.1	11	0.1	-77	1
VD9	0.01	101	Cal	0.8	4.6	2.7	0.2	13	0.2	21	0.3	-67	1
VD10	0.01	103	Cal	0.86	5.1	2.7	0.2	10	0.2	17	0.2	-61	1
VDL1	51	51	Cal	0.85	5.0	1.1	0.1	1.1	0.1	2.1	0.1	0	0.6
VDL2	51	51	Cal	0.81	4.7	2.5	0.1	2.5	0.1	4.9	0.1	0	0.3
V0	0	0	Cal	0.79	4.5	BD	-	0.01	0.01	-	-	-	-
VD11	0.01	100	Cal	0	-	BD	-	64	2.6	87	2.6	-	-
VL11	101	0.03	Cal	0	-	75	2.4	BD	-	72	2.4	-	-
VL1	129	0.04	OI	0.81	6.2	4.8	0.1	0.21	0.01	3.8	0.1	92	1.4
VL2	110	0.03	OI	0.9	7.1	8.3	0.1	0.32	0.01	7.8	0.1	93	1.4
VD1	0.01	103	OI	0.89	7.0	0.33	0.01	7.6	0.1	7.7	0.1	-92	1.3
VD2	0.02	126	OI	0.9	7.1	0.54	0.01	10.3	0.1	8.6	0.1	-90	1.2
VD3	0.02	109	Hem	0.83	8.1	0.16	0.01	2.1	0.1	2.1	0.1	-86	1.7
VL3	102	0.03	Hem	0.82	8.0	3.4	0.1	0.37	0.01	3.7	0.1	80	1.3
VL12	100	0.03	NC	0	-	85	5.9	BD	-	81	5.9	-	-
VD12	0.01	100	NC	0	-	BD	-	63	0.9	85	0.9	-	-

OI olivine 200 mg, Hem hematite 200 mg, Cal calcite 300 mg, NC natural calcite 300 mg, BD below detection

Fig. 2 Yield (%) of valine in recovered samples of calcite (*blue diamonds*), hematite (*red squares*), and olivine (*green triangles*) as a function of pressure (GPa). Zero pressure data are for analyses of samples obtained from containers without impact using the same method as those from impacted containers

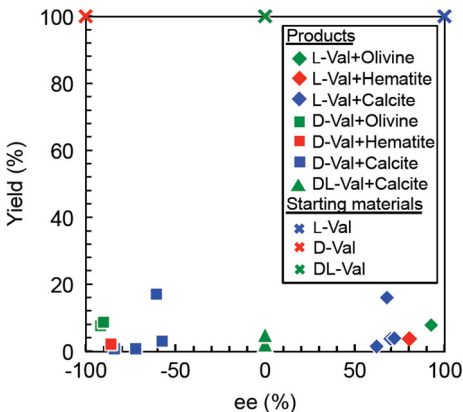


at 0.9 km/s ($n = 2$). The ee of L-valine in experiments with hematite decreased from 100 to 80% following impact at 0.82 km/s ($n = 1$), whereas the ee of D-valine decreased from -100 to -86% following impact at 0.83 km/s ($n = 1$). Considering the standard deviation acquired for experiments with calcite, up to $\pm 10\%$, valine with olivine or hematite also racemized and showed no significant difference in its racemization extent. In summary, following impact-induced heating, valine racemized with no enantiomeric preference with all of the minerals considered. The level of racemization differed for different minerals; calcite provided the highest level of racemization (Fig. 3), while olivine provided the lowest level of racemization.

Discussion

Racemization of dissolved valine by impact-induced heating was found in every experiment with calcite, olivine, and hematite (Fig. 3). The impact-induced heating further decomposed dissolved valine significantly, which is consistent with the results of previous studies (Bertrand et al. 2009; Blank et al. 2001; Peterson et al. 1997; Sugahara and Mimura 2014; Umeda et al. 2016).

Fig. 3 Relationship between yield (%) and enantiomer excess (ee; %) in recovered valine samples. L-Val = L-valine; D-val = D-valine; DL-Val = racemate of valine



Identical impact velocities provided different shock pressures and temperatures in different samples. Impact at 0.81–0.84 km/s generated pressures of 4.8, 6.2, and 8.1 GPa in experiments with calcite, olivine, and hematite, respectively (Fig. 2). Depending on the pressure level, temperature of the compressed solution increased; thus, shock temperature was highest in hematite samples and lowest in calcite samples. Valine with hematite was more significantly decomposed than that with olivine. Furthermore, racemization was also promoted to a greater degree in hematite samples than in olivine samples. This is consistent with the effects of shock temperature; however, the racemization levels of calcite are less dependent on impact pressure and temperature (Fig. 3).

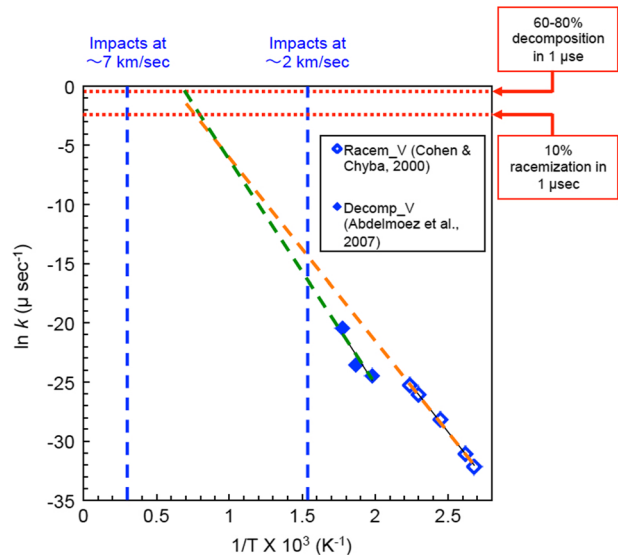
Racemization is promoted in high pH solutions because the high activity of OH^- promotes the removal of H from chiral center (Bada 1972; Smith and Sivakua 1983). The pH of starting material solutions with calcite, olivine, and hematite were ~ 10 , 6, and 6, respectively, assuming that olivine and hematite did not dissolve; therefore, the high pH in calcite experiments would have promoted racemization (Fig. 3).

The XRD analysis of hematite after impact experiments showed the presence of a detectable amount of magnetite. This indicates that oxygen fugacity in the system was close to the hematite-magnetite buffer. Under similar impact conditions, olivine is not oxidized from Fe^{2+} to Fe^{3+} , but just partially altered to form poorly crystalized serpentine (Furukawa et al. 2011; Umeda et al. 2016). This indicates that the oxygen fugacity remained sufficiently low in experiments with olivine. Conversely, the presence of calcite helps to maintain relatively high oxygen fugacity; however, this oxygen fugacity did not have clear relationship to the yields and ee of valine (Fig. 2; Fig. 3).

The experimental range of pressure was ~ 4 –8 GPa, corresponding to vertical oceanic impact velocities of ~ 2 km/s for ordinary chondrites, ~ 2.5 km/s for carbonaceous chondrites, and ~ 3 km/s for comets, based on compiled Hugoniot data (Marsh 1980; Zhang and Sekine 2007). On the other hand, temperatures in the present shock experiments were estimated to be higher than those provided by shock compression, with the additional heat provided by exothermic reactions and friction/sondary impacts of mineral powders due to the presence of an air gap in the sample cavity (Furukawa et al. 2011). In the present results, more than 80% of valine was decomposed, but only 10% of ee changes were found in the residual valine. These results are similar to those of a 20.1 GPa shock experiment with a low water/rock ratio reported in Bertrand et al. (2009). In past studies, rates of decomposition and racemization of valine at lower temperatures have been reported as a function of temperature (Abdelmoez et al. 2007; Bada 1972; Cohen and Chyba 2000). If these rate constants are extrapolated to our decomposition results (60–80% in 1 μsec ; shown as the top red dotted line in Fig. 4) and to our rate of racemization (10% in 1 μsec ; shown in another red dotted line; Fig. 4), a temperature during the shock compression of ~ 1100 °C is indicated. This is consistent with estimates from our previous study (Furukawa et al. 2011), which implies that shock-induced pressure is not significantly affected by the rate constant of racemization and decomposition of dissolved valine under the present experimental conditions.

The final impact velocity of natural impacts on the Earth's surface depends on the initial velocity, size of the meteor, and terrestrial atmospheric pressure (Hills and Goda 1993). According to a previous study, small projectiles ($<10^8$ g) burst in air and decelerate, while projectiles with greater mass reach the Earth's surface at a significant fraction of their initial velocity (11–30 km/s) and impact the Earth at hypervelocity (Anders 1989). The shock pressures and temperatures in the present study are not as strong as those expected for natural hypervelocity impacts because of technical difficulties associated with sample recovery. Based

Fig. 4 Rate constants of racemization and decomposition compiled from Cohen and Chyba (2000) and Abdelmoez et al. (2007). In-shock temperatures of the impact of ordinary chondrite to water are denoted by blue dashed lines, as estimated from known Hugoniot data. Green and orange broken lines denote extrapolated trends for the rates of decomposition and racemization of valine, respectively. Red dotted lines denote the rates of decomposition and racemization for valine by shock compression in the present study



on the present results and on the kinetic data considered (Fig. 4), amino acids in shocked ocean may have been completely decomposed in natural hypervelocity impacts by large objects (>10-m projectile with >10 km/s). On the other hand, in the impacts of decelerated projectiles (velocities less than a few km/s), the rate of racemization may have exceeded the rate of decomposition (Fig. 4). However, even if we take into account inclined impacts, impacts at a few km/s are rare in the population of projectiles because of fragmentation and aerodynamic braking in the Earth's atmosphere (Hills and Goda 1993). Projectiles with lower velocities have smaller mass (e.g., <10 kg; (Hills and Goda 1993); therefore, the duration would not have been sufficient for significant racemization to occur.

Residual heat, which is also characteristic of hypervelocity impacts (Sharp and DeCarli 2006), remains after adiabatic release from the shock compression and escapes from the system through thermal conduction. The duration of this heat is much longer than heating during shock compression, and depends on projectile size and distance from the impact site. In hypervelocity impacts, the heat generated during the shock compression may have decomposed all amino acids before residual heating. Although residual temperatures in porous targets can rise significantly with porosity, it is generally lower than the temperature rise by shock compression; therefore, in impacts by decelerated projectiles (<10 km/s), the effect of residual heat could be negligible (i.e., both decomposition and racemization are low). Based on our results, we conclude that successive impacts of asteroids and meteorites may have decomposed some oceanic amino acids, and that the racemization of proteinogenic amino acids accumulated in entire ocean was probably negligible.

The ee of proteinogenic amino acids in meteorites may be smaller than non-proteinogenic amino acids or even negligible in some cases, since they are more easily racemized than amino acids having no hydrogen atom on the α -carbon (Pollock et al. 1975). However, this conclusion implies that if chiral proteinogenic amino acids were provided from space and accumulated in oceans, the ee would not have completely disappeared by successive impacts.

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